Self-Assembled Monolayers

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The Rate of Charge Tunneling through Self-Assembled Monolayers Is Insensitive to Many Functional Group Substitutions[**]

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At its conception, the field of molecular electronics promised to provide the ability to engineer the rate of charge transport through the design of the molecular structure of electronic junctions.[1] The hypothesis was that the electronic and geometrical structure of molecules in a junction would have a significant and predictable effect on the rate and mechanism of charge transport through their influence on the energetic topography of the tunneling barrier. Here we show the preparation and electrical characterization of junctions (Figure 1) with the structure $Ag^{TS}/S(CH_2)_4CONH(CH_2)_2R//Ga_2O_3/EGaIn$ (Ag^{TS} = template-stripped silver surface;[2] R = tail group; EGaIn = eutectic gallium and indium alloy; Ga_2O_3 = a passivating metal oxide film on the surface of the EGaIn[3–5]) containing a range of common aliphatic, aromatic, and heteroaromatic organic tail groups. We demonstrate that the rate of charge transport across these self-assembled monolayers (SAMs) is surprisingly insensitive to changes of the organic molecules of which they are composed. This study is based on a physical-organic design: that is, the information it provides comes from comparisons of rates of tunneling across related structures, rather than from the interpretation of the absolute values of single measurements.

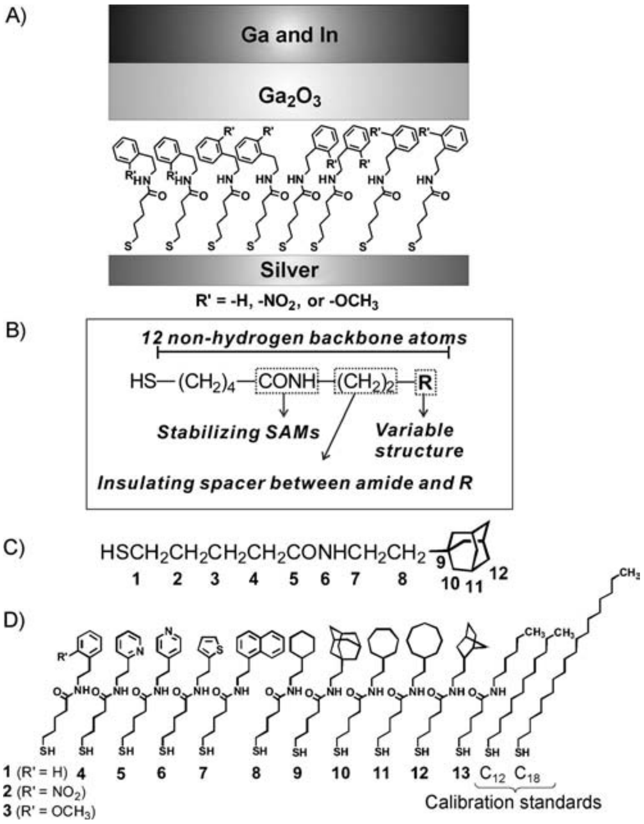

Figure 1. A) Schematic representation of a tunneling junction consisting of a template-stripped Ag bottom electrode supporting a SAM, and contacted by a Ga_2O_3/EGaIn top electrode. B) A schematic representation of one junction. C) The numbering system based on non-hydrogen atoms in the backbone of the molecules tested. D) Molecules used to form SAMs for this study.

Targets for shaping the tunneling barriers of molecular junctions have included electron-donor/bridge/electron-acceptor molecules,[1a,6] molecular quantum dot systems,[7] aromatic molecules,[8] and complex organic molecules with multiple functional groups.[9] Many of these studies ostensibly shaping the tunneling barriers of molecular junctions have, however, been difficult to interpret because, when they were carried out, there were no experimental systems that generated well-characterized, statistically validated data. We characterize herein the rates of charge transport by tunneling across a series of molecules—arrayed in SAMs—containing a common head group and body ($HS(CH_2)_4CONH(CH_2)_2$-) and structurally varied tail groups (-R). These molecules are assembled in junctions with the structure $Ag^{TS}/SAM//Ga_2O_3/EGaIn$. Changing the structure of R over a range of common aliphatic, aromatic, and heteroaromatic organic tail groups does not significantly influence the rate of tunneling. In making these measurements, we utilize C_{12} and C_{18} alkanethiols as calibration standards to allow comparison with results from other types of junctions.

Limited studies[4,5,10–15] of charge transport using a range of junctions have described the relation between molecular

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structure and the rate of tunneling. For example, Venkataraman et al.[14] reported that the rate of charge transport through a series of diaminobenzenes depends on the alignment of the metal Fermi level with the closest molecular orbital. Chiechi, Solomon et al.[15] compared the rate of charge transport through three different anthracene derivatives of approximately the same thickness, and concluded that conjugation influences the rate of charge transport. Studies exploring the correlation between molecular structure and charge transport based on systematic physical-organic measurements of the rate of charge transport over a wide range of structures are sparse. We describe herein tunneling rates through SAMs of molecules with a variety of molecular structures, including aromatic, heterocyclic, and aliphatic moieties. We have previously examined ferrocene-terminated SAMs[4] and SAMs with odd- and even-numbered *n*-alkanethiolates.[5]

Most of the molecules used in the SAMs of this study were designed to have three features (Figure 1b): 1) The total number of non-hydrogen atoms from the sulfur (head) to the most distal point of the tail is 12 (Figure 1c). This constant length allows us to compare values of tunneling currents across these SAMs directly, with no (to a first approximation) corrections for differences in the width of the tunneling barrier. It also gives conveniently measured values of J(V)—the current density ($\mathrm{A\,cm^{-2}}$)—across SAMs at nondamaging values of applied potential. 2) The molecules contain a constant amide group (-CONH-); inclusion of this group increases the yield of nonshorting junctions (typically to 85–100%) and the stability of the system, relative to junctions prepared from *n*-alkanethiols.[16] The internal amide also increases the synthetic accessibility of these molecules: the requisite thiols are easily synthesized in synthetic sequences generally comprising only three steps (see the Supporting Information). 3) A -CH_2CH_2- unit adjacent to the terminal R group insulates it electronically from the amide.

For the tail groups R, we included: 1) aromatic (**1**–**7**) and aliphatic (**8**–**13**) groups; 2) aromatic groups with different structures and patterns of substitution; 3) aliphatic compounds with different degrees of conformational flexibility (**8**–**12**); and 4) groups capable of interacting with the top electrode through donor–acceptor interactions (**2**–**7**).

We built the molecular junctions by using SAMs on ultraflat Ag^{TS} substrates and with liquid–metal (EGaIn) top electrodes by following the procedure for fabrication reported previously (see the Supporting Information for details).[3–5]

Charge transport is insensitive to many structural changes. Figure 2 summarizes data describing the rate of charge transport through molecules **1**–**13**; Table S1 (in the Supporting Information) summarizes information supporting these data. We note four major features: 1) Values of $\langle \log|J| \rangle$ are independent of the structure within the group **1**–**7**. The values of $J(V=0.5\ \mathrm{V})$ are not statistically different from that of the C_{12} thiol standard. 2) None of the compounds has a rectification ratio greater than 1.4 (Table S1).The small rectification that is observed is likely due to some feature of the junction (for example, differences in work function or features of the S-Ag and R//Ga_2O_3 interfaces), not to the molecules of the SAMs. 3) The value of $\langle \log|J| \rangle$ for compound **13** is not distinguishable from that of the C_{12} thiol, although the compounds differ in the substitution of a -CONH- group (**13**) for a -CH_2CH_2- group (C_{12}).[17] 4) Aliphatic compounds **8**–**13** show slightly lower (by a factor of 4) values of J(V) as the size of the group R increases, perhaps because the thickness of the monolayer increases slightly with bulky groups.

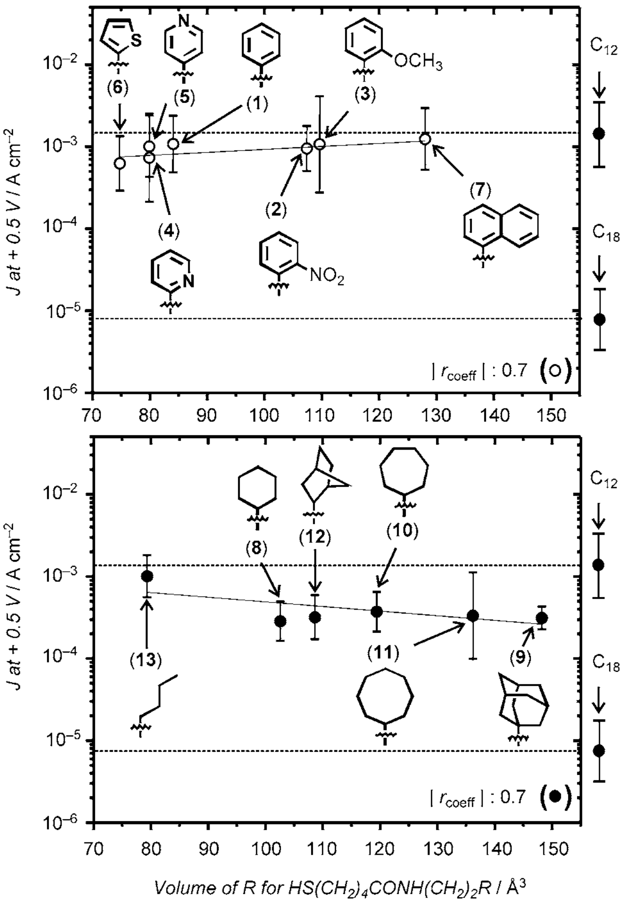

Figure 2. Plots of current densities of amide derivatives **1**–**13** (in Figure 1) and two calibration standard alkanethiols, 1-dodecanethiol (HS-$(CH_2)_{11}CH_3$, C_{12}) and 1-octadecanethiol (HS-$(CH_2)_{17}CH_3$, C_{18}), as a function of volume of the corresponding aromatic and aliphatic tail group (R for $HS(CH_2)_4CONH(CH_2)_2R$). The dashed lines represent the tunneling current for the calibration standards (C_{12} and C_{18} alkanethiols), and the solid lines are linear squares fits. The molecular structures shown are those of the tail groups R. The r_{coeff} is a correlation coefficient for each scatterplot. The molecular volumes of the tail groups were calculated from the Molinspiration Property Calculation Service at http://www.molinspiration.com. ○: aromatic moieties, ●: aliphatic moieties.

In this study, the structure of the tail group R was varied over a range of structures used typically in organic chemistry, while maintaining an approximately constant thickness of the tunneling barrier. The span of the rates of tunneling current was less than a factor of approximately five over the entire series ($-3.6 \leq \langle \log|J| \rangle \leq -2.9$). This very small response of the charge transport to the structure of R suggests that the rates of tunneling through SAMs are largely insensitive to differences in the electronic structures of R.

Casual inspection of the plots of J(V) in Figure 2 suggests that there are trends: the J(V) value for aromatic moieties appears to increase as the volume of R increases, while the J(V) value for aliphatic moieties appears to decrease. Statistical analyses, however, indicate that these trends are not statistically significant—more specifically, the slopes of the linear least square fits are not statistically significantly different from zero at the 95% confidence level (see the Supporting Information).

The rates of tunneling show a range of responses to the molecular composition of the SAMs, and there is still no single theory that integrates and rationalizes all of these responses. We,[5] Waldeck and co-workers,[11] and Lee and co-workers[12] have previously observed the effect of the interface between the metal electrodes and the molecules on the value of J(V): an odd-even effect[5] in SAMs composed of *n*-alkanethiolates, and the influence of metal–molecule contacts[11,12] in metal–molecule–metal junctions. Others[12,15] have reported that conjugation of aromatic units has a large effect on tunneling rates, as do changes in the structure of aromatic groups in the SAM. SAMs composed of ferrocene-terminated *n*-alkanethiolates show significant rectification of current ($r \approx 100$).[4]

At present it is unclear how to rationalize, for example, the observation of an odd-even effect in *n*-alkanethiolates[5] with the observation that substitution of R = cyclohexyl by R = phenyl produces only an increase in J(0.5 V) of a factor of only about four (a value which might reflect only a small change in the thickness of the SAM). Indeed, the odd-even effect demonstrates that a small change in the molecular structure of the components of a SAM can influence the rate of charge transport across it,[5] while the change from cyclohexyl to phenyl demonstrates that a large change need not do so. This study does not discount the idea that certain structural changes may change the rates of charge transport.[4,11–13,15] It suggests that changing the functional groups to others normally examined in physical-organic chemistry (hydrocarbons, amides, simple aromatic moieties) will be insufficient to produce large changes in J(V) for SAMs of the same thickness.

At the advent of molecular electronics, it seemed possible that relatively "small" changes to the structure of the SAM (e.g. changes in the dipole moments, aromaticity, polarizability, conductivity of the assembled molecules, or groups in them) would significantly change the rates of charge transport by tunneling across them, and result in unusual J(V) characteristics, unusual conductivity, or high rectification. Figure 2 (and Table S1) suggests that, over a range of structures typical of those used in conventional organic chemistry, changing the structure, for a constant thickness of the SAM, has little influence on the rates of tunneling. This conclusion indicates that the rate of charge transport can be modeled by tunneling through a rectangular barrier whose structure at the atomic/molecular level is not important. To summarize this conclusion in colloquial terms would be to say "it's all fat".

This study has five useful features: 1) It improves intuition concerning the types of molecular structures that influence the rate of charge transport across thin, insulating organic films; 2) it outlines a method to improve the accuracy and reliability of the measurement of J(V) values by interspersing calibration standards among measurements of new compounds; 3) it provides an extensive set of comparable data against which to test theories of charge tunneling in organic matter; 4) it will restrain the enthusiasm of speculation about the range of exotic electronic effects that may be achieved by engineering the structures of organic tunneling barriers; and 5) in combination with other studies,[4] it will suggest directions for research involving functional groups having electronic structures that will, in fact, influence rates of tunneling.

The results described here combine with previous results[4,5,11–13,15] to begin to define the types and energies of orbitals required to influence sufficiently the shape of tunneling barriers so as to influence the rate of tunneling across them. The results in Figure 2 thus provide an important guide for future research in the field of molecular electronics.

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[17] We have recently completed a systematic study on charge tunneling through a series of SAMs composed of either aliphatic thiolates or amide-containing thiolates; this study further supports the hypothesis that the rate of charge tunneling through SAMs is insensitive to the replacement of a -CH_2CH_2- group with a -CONH- group.